THE SYNTHETIC OR CATALYTIC MODIFICATIONS IN THE OIL DISTILLATE FROM THE LOW TEMPERATURE COKING OF COAL

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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THE SYNTHETIC OR CATALYTIC MODIFICATIONS IN THE OIL DISTILLATE FROM THE LOW TEMPERATURE COKING OF COAL.

I. INTRODUCTION.

1. General survey of the field. Coal tar is the product which condenses from the gases formed in the carbonization of certain suitable coals. The raw tar is composed of light oils, pyridene bases, phenols, napthalene, anthracene, heavy oils, complex organic compounds insoluble in benzene, known as free carbon, water, and ammonia. Of this tar about 10% can be made into drugs and dyes, while the other 90% is suitable for the manufacture of pitches and various heavy oils. Advantageous commercial disposal of this 90% of the tar is therefore of great importance. The production of tar in the United States has had a remarkable growth in the last few years. The production since 1908 is as follows:-

1908	99,000,000 gallons.
1912	132,000,000 gallons.
1913	155,000,000 gallons.

About 75% of the production in 1913 was from by-product coke ovens. The remainder was by-products in the manufacture of coal gas in gas retorts and in gas producers in which bituminous coal is used.

Coal tar is separated by distillation into a number of fractions. The fractions generally made are, light oil which is taken up to 160°, middle oil from 160 to 230°, heavy oil from 230 to 350°, and pitch above 350°. Light oil is used for solvents, cleansers, pitch-paint thinners, gas enrichment , and is the source of aniline dyes, nitro-compounds used in explosives, various photographic chemicals, medicines, and drugs. Middle oil is used as a source of creosote oil, phenol, disinfectants, nitro-compounds for explosives, napthol dyes and colors, and artificial indigo. Heavy oil is used as a source of creosote oil, naptlalene,

anthracene, road oils, alizarin and alizarin dyes. The pitch finds application as road binders, roofing pitches, for briquetting finely divided fuels, and its use as an electrical insulating material is being developed. The supply of creosote oil for the impregnation and preservation of wood comes almost entirely from coke-oven tar and the present supply does not meet more than one-third of the demand. This shortage in the supply can be met only by the increase of by-product coking operations and by establishment of new coal distillation processes especially adopted to the recovery of by-products.

Since the war Germany has lacked oils of all kinds. Lubricating oils which are now used are for the most part mineral oils extracted from petroleum and largely imported from America. It would be very advantageous then for Germany to be able to extract the lubricants which she needs from the coal by distillation. This, then, has led to a minute study of coal distillation at low temperatures. In England some companies were formed for the distillation of coal at low temperatures, among others the Coalite Company, which obtained very large yields of tar and a semi-coke which can be used as a domestic smokeless fuel. In America much work has been done on low temperature processes, but as yet they have had no industrial application.

2. Resume of previous investigations. There are two principal types of coal-tar, namely low-temperature tar and high-temperature tar. The former has been shown[1] to be a primary product in the distillation of coal and the latter a secondary product, being formed to a great extent by the decomposition of low-temperature tar. Work on the low-temperature process is comparatively recent, although the knowledge of the effects produced by varying the temperature of the coking process has been known for some time. Wright[2] in 1888 showed the effect of increase of temperature in a very striking manner. He subjected five samples of the same coal to distillation at increasing temperatures, and obtained the following results.

Table 1.

Analyses of tar obtained at varying temperatures.

	No.1 600°	No.2 650°	No.3 700°	No.4 750°	No.6 800°
Specific gravity	1.084	1.103	1.149	1.154	1.204
Gas yield, Cu. ft. / ton	6600	7200	8900	10,162	11,700
Free carbon, per cent	8.69	11.92	15.53	19.78	24.67
Crude naptha	9.17	9.05	3.73	3.45	0.99
Light oil	10.50	7.46	4.47	2.59	0.57
Creosote oil	26.45	25.83	27.29	27.33	19.44
Anthracene oil	20.32	15.57	18.13	13.77	12.28
Pitch	28.89	36.80	41.80	46.67	64.08
Paraffin in naptha	5.00	4.00	1.50	1.50	1.00

Davis[3] in discussing the tars formed under different temperature conditions says that at low temperatures are produced such hydrocarbons as belong to the paraffin series having the general formula C_nH_{2n-2}, along with the olefines C_nH_{2n}. The lower members of these series are liquid and in the pure state are lubricating oils, the higher ones are solid and form commercial paraffin. They are always accompanied by phenols. At high temperatures the olefines and

acetylenes occur more or less, but the paraffins disappear almost completely with the decomposition of carbon. The action of heat causes molecular condensation by which compounds of higher molecular weight are formed such as napthalene and anthracene.

Lewes[4] showed that tars produced at temperatures between 400-500°C. contain relatively low percentages of aromatic substances and high percentages of the paraffin series which are adopted to use as motor oils. The middle oils are free from napthalene and yield excellent enriching oils. The pitch has practically no free carbon and would form an ideal electric insulating material.

Jayne[6] shows the influence of temperature upon carbonizing very strikingly by the test of two tars, both made on the same coal, and in the same kind of ovens. The high temperature tar had a specific gravity of 1.21 and tested 17.5 percent of free carbon; the light oil fraction was 2.20 percent of a gravity of 0.979, testing 23% to 170 degrees, the pressed napthalene yield was 7.4 percent. The low-temperature tar had a specific gravity of 1.137, and testing 3.2 percent of free carbon, the light oil amounted to 11.9 percent, and had a gravity of 0.970, testing 28 percent to 170 degrees, the total tar acids were 12.48%, while the pressed napthalene fell to 1.2 percent. He thinks that in the first tar the light hydrocarbons and tar acids have been destroyed by the temperature employed, with the formation of napthalene. Bornstein[6] subjected eight Westphalian coals to a maximum temperature of 450° and stated that the tars had a specific gravity of from 0.95 to 0.98, began to distill at about 70-80°, and were found to contain no aniline, thiophene, napthalene or anthracene. He gave the solid paraffin content as from 0.3 to 2.0 percent.

Parr and Francis[7] worked on low temperature processes with the purpose of modifying the volatile matter, either in amount or form, so that a smokeless fuel and a fuel of higher rate of efficiency in combustion would result.

Church[8] of the Barrett Company has compiled a table or results of analyses which were made in his laboratory, of the typical coke-oven tars produced in the United States.

Table 2.

Analyses of Typical Tars; Dry Tar

	Gas Retort		Coke Oven			
	Horizontal	Inclined	Vertical.	United Otto	Semet Solvay	(ers Kopp-
Specific gravity	1.266	1.238	1.153	1.207	1.188	1.186
Free carbon	28.8	24.3		13.3	10.7	6.80
Specific viscosity (Engler at 100°)	21.8	14.9	2.10	3.40	3.0	2.10
Oil distillate	13.2	14.3	28.80	21.2	21.8	35.3
Pitch residue	86.8	85.7	71.2	78.8	78.2	64.7
Tar acids	14.0	21.0	29.0	12.0	4.0	0

These figures are of especial interest when they are compared to those of low-temperature tars as given in Table I.

Dunstan[9] states that the tar produced by the low-temperature carbonization and under vacuum differ from common tars in the following respects:- (1) larger amount of light oils, (2) absence of napthalene and solid volatile products, (3) absence of phenol and the presence of a large amount of cresylic acid homologues, (4) less free carbon and a better quantity of pitch. The benezoid compounds are absent and their place is taken by paraffinoid and unsaturated derivatives. The yield of tar is higher and the light oil would rectify into motor spirits, solvent, and burning oils, and the higher fractions would contain valuable disinfectants. They would also serve as excellent creosoting oils.

Jones and Wheeler[10] in their study of low-temperature carbonization give an analysis of the tar as follows:- 40-45% of unsaturated olefines, 40% of napthenes and paraffins, 12-15% of tar acids, 7% of aromatics, traces of pyridenes, and small quantities of solid paraffin.

Parr and Olin[11] in their study of the low temperature process find that tar is rich in low boiling distillate, the pitch residue is small, there is a high percentage of tar acids, napthalene is absent, and the free carbon in the tar is less than 2%.

They give the following results of their tar analysis:-

Table III

Results of Preliminary Distillation of Tar.

Fraction	Temperature range	Percentage
Light oil	Below 210°	17.2
Heavy oil	210-325°	52.7
Pitch	above 325°	30.1

Table IV

Light Oil Fraction (to 210°)
Specific gravity 0.966

	Percentage on basis of crude tar	Percentage of basis of of light oil fraction
Light oil fraction	17.2	100.
Phenols (tar acids)	5.7	33.0
Amines (tar acids)	0.9	5.3
Paraffins	3.12	18.1

Table V

Composition of Heavy Oil (210-325°)
Specific gravity 1.032

	Percentage on basis of crude tar	Percentage on basis of heavy oil fraction
Heavy oil fraction	52.7	100.
Tar acids	22.2	42.13
Paraffins	6.2	32.66
Napthalene	.0	.0
Anthracene	.0	.0

Table VI

Pitch Fraction

Percentage on the basis of crude tar	30.1
Melting point	110.0
Specific gravity	1.27
Free carbon, percent	12.00

Weiss[12] has worked out the most complete set of methods of analysis for tars, but all his methods are of use on high temperature tar, and must therefore be modified for application to low-temperature tar.

Parr and Layng[13], coking coal at a temperature of 750°, give the following analyses of the tars:-

Table VII

Types of Tars from Low-temperature Carbonization.

Coal	Free Carbon Percent	Percent Distillation Up to 190°C	190-300°	300-360°	Pitch	Percent Fractions Tar Acids	Amines	Paraffins
Illinois	1.8	2.8	33.8	24.4	38.9	45.0	3.6	8.0
Illinois	0.5	1.4	41.3	32.8	24.5	45.0	3.0	10.0
Illinois	0.5	1.5	41.9	33.8	19.8	47.0	4.0	10.0
West Virginia	0.5	2.0	41.0	31.0	26.0	40.0	4.0	12.5
West Virginia	0.5	2.0	36.5	31.0	30.5	36.0	4.0	12.4
Pennsylvania	5.5	0.0	29.4	30.9	39.7	20.0	8.0	12.0
Pennsylvania	10.7	0.0	24.0	33.2	42.8	20.0	6.0	10.0

3. Purpose of this investigation. As the principal object of coking coal is not for the production of tar, there has been but little investigation of the conditions necessary to produce tars of the most desirable properties. There has also been but little investigation of the tars which are produced to render them of more value to the tar distiller. In considering new sources of supply of coal tar regard must be had of certain new processes of coal distillation, notably low-temperature carbonization. By distilling at 600 to 800° coals that coke moderately well, excellent yields of tar may be obtained with fair yields of ammonia and fuel gas. The semi-coked residue is valuable as a domestic smokeless fuel. The tars produced at low temperatures have a very different composition from common tars and together with the fact that the amount of tar is increased from about eight gallons per ton to about twenty gallons, the importance of their economical commercial valuable utilization is apparent. The principal differences between low and high-temperature tar is that low-temperature tar has a very low percentage of free carbon, has a large amount of tar oils, and low pitch content, low in aromatics, high in phenols, high in paraffins, high in aliphatics, and it contains a large percentage of unsaturated compounds. Methods of analysis for high temperature tars have been fairly well worked out, but as yet no good scheme of analysis has been worked out for low-temperature tars. It is the purpose of this investigation to show the differences between the two tars and to give suitable means of determining these differences. The unsaturated compounds of low temperature tar depreciates its value from the standpoint of the tar distiller, because they absorb oxygen from the air very easily and form dark, foul smelling compounds, and because they cause a loss upon distillation. These compounds can be removed from the

tar by sulfonation, but this process would cause too great a loss of the distillate. The possibility of saturating these compounds with hydrogen suggests itself and this method of improvement was investigated.

II. EXPERIMENTAL ON TARS.

1. Tars used. The tars used were obtained by Mr. H. E. Hyde and Mr. O. Holzman from the carbonization of Illinois coals at low temperatures in the experimental coking plant in the Department of Chemistry at the University of Illinois.

2. Apparatus used. The tars were dehydrated and fractionally distilled in a specially constructed electric furnace, having a temperature range of from room heat up to 500°C. With this furnace it was possible to heat the tars evenly on all sides at once, with a minimum of cracking and foaming over. "Pyrex" side-necked distilling flasks were used along with a thirty inch water condenser up to 200°, and above that an air condenser was used.

3. Methods of analysis. All of the tars received contained a high percentage of water and it was necessary to remove this before they could be analyzed. This water was removed by carrying the distillation to a point where the vapor temperature reached 210°. The distilled oil is separated from the water and returned to the flask after the latter has been cooled to a moderate temperature. This temperature is used because it is sufficiently high to expel all water from the flask. In the first three distillations the distillate was cut and weighed at every ten degrees to see whether there was any natural stopping place and to see whether there was a large percentage of any certain compound or class of compounds which should be taken off in one fraction. All remaining distillations were made cutting at the temperatures determined in the above three distillations. Specific gravities were taken at 25-30° and then corrected to 15.5°C. As there was but a small portion of each fraction they were all combined and the tar acids determined on the entire distillate. 50cc. of the oil was shaken

in a separatory funnel with successive 50cc. portions of 10 percent caustic soda solution until no more tar acids were removed. The remaining oil is washed with water to remove the alkali, the water drawn off and the contraction in volume taken as the tar acid content. Free carbon was determined by extraction first with benzene and then with toluene in a soxhlet extraction apparatus.

4. Presentation and discussion of data.

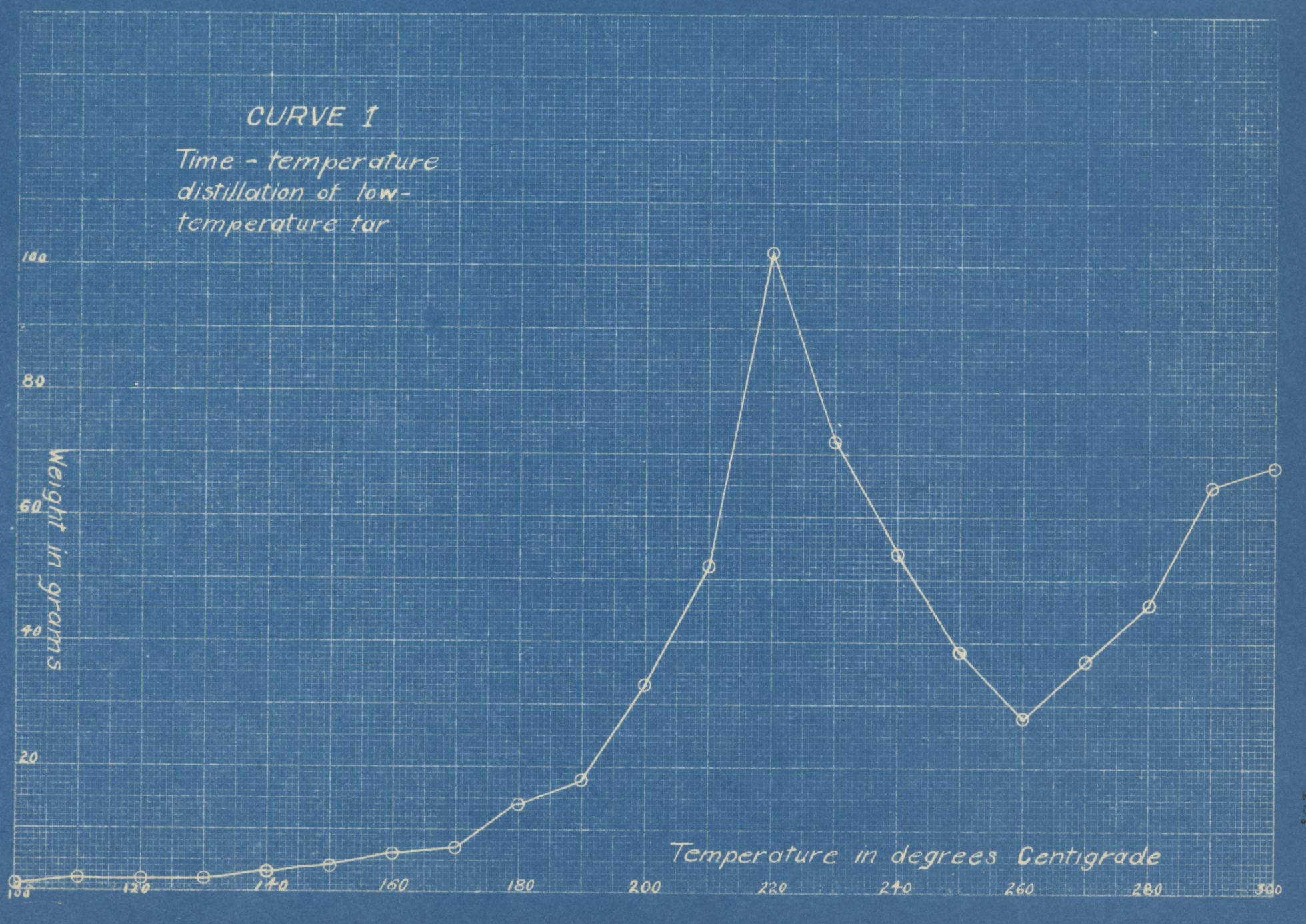
Table VIII.

Temperature-Weight Distillation of Low-Temperature Tar.

Temperature	No. 1	No. 2	No. 3
Up to 80°	0	0	1.0
90°	1.0	0.5	1.0
100°	1.0	1.0	1.0
110°	2.0	1.0	1.0
120°	2.0	1.0	1.0
130°	2.0	1.0	1.0
140°	3.0	1.0	1.5
150°	4.0	1.0	2.0
160°	6.0	2.0	2.5
170°	7.0	2.0	4.5
180°	14.0	3.0	7.0
190°	18.0	4.0	8.0
200°	33.0	10.0	14.0
210°	52.0	31.0	26.5
220°	102.0	71.0	53.0
230°	72.0	30.0	38.0
240°	54.0	22.0	17.5
250°	38.5	18.0	20.0
260°	28.0	12.0	14.0
270°	37.0	17.0	21.0
280°	46.0	33.5	24.0
290°	65.0	32.0	25.0
300°	68.0	46.0	32.0

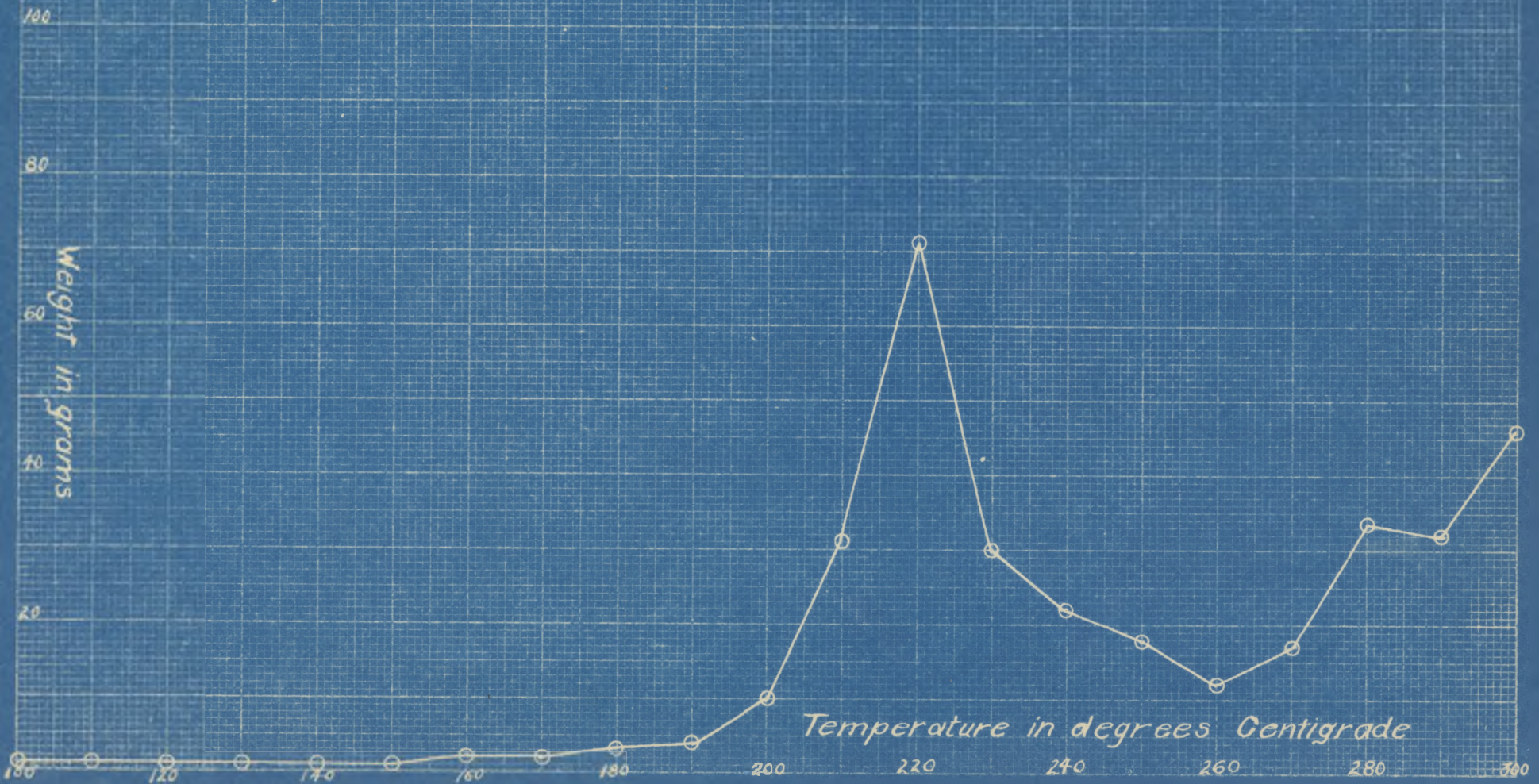
CURVE 1

Time - temperature distillation of low-temperature tar



CURVE 2

Time - temperature distillation of low-temperature tar



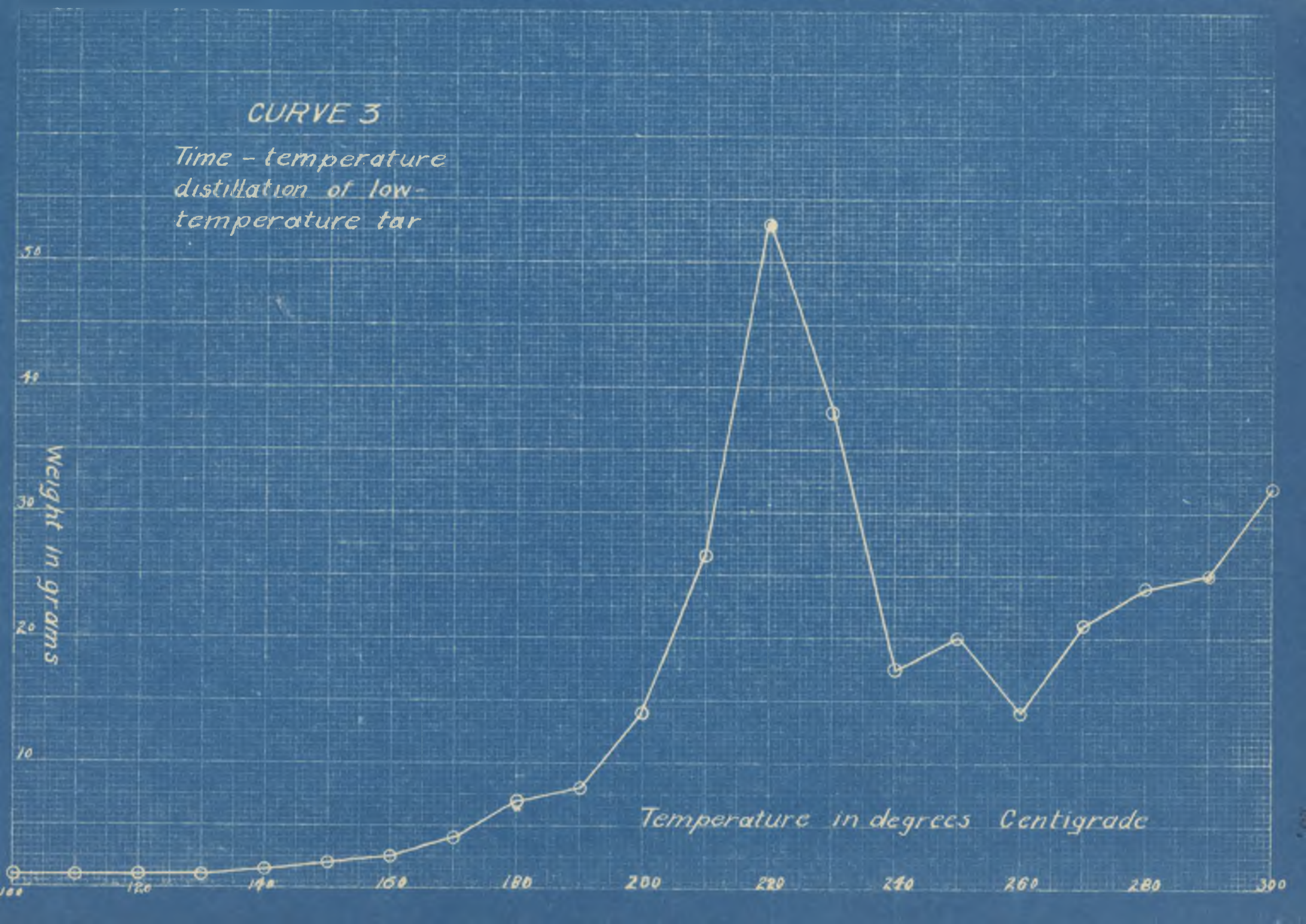

CURVE 3
Time - temperature distillation of low-temperature tar
50
40
30
20
10
Weight in grams
160
180
200
220
240
260
280
300
Temperature in degrees Centigrade

Table IX

Percentage Composition on Basis of Dry Tar.

Fraction	No. 1	No. 2	No. 3
Up to 220°	23.7	23.7	25.3
220 to 260°	18.9	16.2	18.1
260 to 300°	20.4	25.4	20.6
Pitch	37.0	34.7	36.0

Table X

Table of Analysis

	No. 1	No. 2	No. 3
Tar acids, per cent of distillate to 300°	---	31.5	33.8
Free carbon, percent of dry tar	1.11	1.19	0.78
Specific gravity of dry tar at 15.5°	1.056	1.066	1.052

From the results given in Table VIII it was shown that there were two abrupt drops in the curves which were obtained by plotting the weight of distillate against the temperature. Cuts were made at every ten degrees and curves 1, 2, and 3 all show the breaks at the same points, namely at 220° and 260° and in all other distillations cuts were made at these points.

In table IX in given the percentage composition of the various fractions obtained from the distillations as recorded in Table VIII. The fraction up to 220° ranges from 23.7 to 25.3 percent, the fraction from 220 to 260° ranges from 16.2 to 18.9 percent, the fraction from 260 to 300° ranges from 20.4 to 25.4 percent, while the pitch is remarkably low ranging from 34.7 to 37.0 percent.

Table X shows that the tar acids are high, that the percentage of free carbon is low, less than 1.5 percent, and the specific gravity has a small range between 1.052 and 1.066.

No further analyses were made excepting the fractioning of the oil into the determined cuts as it was desired to use the distillate for another line of investigation.

Table XI.

Percentage Composition on Basis of Dry Tar.

Number	Up to 220°	220 to 260°	260 to 300°	Pitch
4	24.5	14.35	19.25	41.9
5.	24.4	18.9	16.1	41.1
6	17.0	22.0	17.1	34.3
7	22.8	10.9	20.7	45.6

This Table shows practically the same things that are shown in Table IX, excepting that the percentages are not quite as regular, but their average is practically the same.

EXPERIMENTAL ON HYDROGENATION.

1. Resume of previous investigations. The large amount of unsaturated compounds would immediately suggest the possibility of hydrogenating them, using similar methods to those employed in the soap and fat industries.

Parr and Olin[11] state that the Iodine numbers of the lower fractions of low-temperature tar have been found to be as high as 165. They, however, state that the Iodine number of the distillates is not a true index of the amount of unsaturation as it represents other activities than simple oxidation in such a complex mixture where members of the aromatic series are present. They suggest the possibility of utilizing the lower fraction as drying oils.

In 1823 Doberiner[12] discovered that hydrogen and oxygen would unite to form water when they were passed over spongy platinum. It was also shown by Liebig[13] that platinum black absorbed 800 times its volume of oxygen and that when brought into contact with hydrogen, 310 volumes were taken up, 200 of which united with the oxygen to form water, while the remaining 110 volumes were absorbed. Later it was shown that not only platinum, but other rare metals possessed this property of causing hydrogen and oxygen to unite to form water. Saytzeff[14] in 1871, while working under Kolbe, succeeded in reducing nitro-benzene to aniline by passing a mixture of the vapors of nirto-benzene and hydrogen over palladium black.

The first use of the base metals in catalytic reduction was by Mond[15] in 1888. He found that upon passing gaseous hydrocarbons over metallic nickel at a temperature of from 350° to 400°, or over metallic cobalt at from 400° to 450° carbon was the

final reduction product.

In 1896 Sabatier and Senderns16 began a study of catalysis which resulted in a standard text on the subject of catalytic hydrogenation. They used a number of both base and rare metals. as catalyzers. They showed nickel to be one of the most effective of the base metals as a carrier of hydrogen. They also showed the reaction to be capable of very general application to the field of organic chemistry. All of their reductions were carried carried out in the gaseous state.

The first disclosure of the possibility of hydrogenating in the liquid state apparently came from LePrince and Sivekel7 who merely heated oleic acid on a water bath, mixed with finely divided nickel, and passed a current of water gas or hydrogen through the heated mass. The oleic acid was completely converted into stearic acid. They also converted olive and linseed oils into hard, tallow like masses.

Ellis[18] who has done much work on hydrogenation, has written the latest book on the hydrogenation industry. He has, however, just gathered together all the previous literature on the subject and left the reader to draw his own conclusions as to the selection of that which should prove of the greatest utility.

The only reference to the application of hydrogenation to mineral oils is that of Woodruff and Day19. They carried out hydrogenation of shale oil at a temperature of 750 to 800°F. and a pressure of from 70 to 80 pounds using palladiumized nickel as a catalyzer. Shale oils on ordinary redistillation yields oils ranging from 17 to 24° Baume, where in the hydrogen distillation under pressure they ranged from 24.4 to 39.7° Baume.

2. Oils used. The oils used in all of the work on hydrogenation was the distillate obtained from the tars which have been described.

3. Apparatus used. A specially constructed apparatus was used for the experimental hydrogenation work. Essentially it consists of an electric furnace with the necessary valves and fittings for the control of oil and hydrogen. The heating zone was made from a 2 inch pipe, 36 inches long, by first covering it with a 1/2 inch layer of alundum cement, winding 32 feet of No. 14 Chromel wire about it, and then applying another thin coat of alundum cement. The ends were fitted with two inch flange unions so that the interior could be easily gotten at. The lower union is bushed out to a 1/4 inch pipe provided with an outlet G for draining the apparatus, and an inlet pipe with valve H for control of the incoming hydrogen. A short 1/4 inch capped pipe with four small holes for admitting the hydrogen, is fitted on the inside of the lower union and it extends about 2 inches into the lower part of the furnace. The upper union in fitted with a 2 by 2 inch nipple, and that in turn is fitted by a 2 inch tee, from the top of which a 3/8 inch capped pipe (t), 24 inches long extends into the furnace and serving as a pocket for the thermocouple. A resevoir (K) of about two liters capacity is used and it is fitted with a gauge glass (L) for measuring the amount of oil present in the resevoir. A sight-glass J is provided between the resevoir and the furnace, so that the flow of oil can be more evenly regulated. The outlet for the excess hydrogen is fitted with two control valves E and D and a eudiometer for measuring the pressure within the apparatus. The pressure is regulated by means of valve E, and a water seal is used to prevent the entrance of air into the apparatus. The furnace is insulated with a five inch layer of "Sil-O-Cel" contained in a 14 inch can which is placed around the furnace. The whole apparatus is supported by a frame work made of 3/4 inch pipe. The voltage used for heating the furnace was 110 volts and the temperature was regulated by means

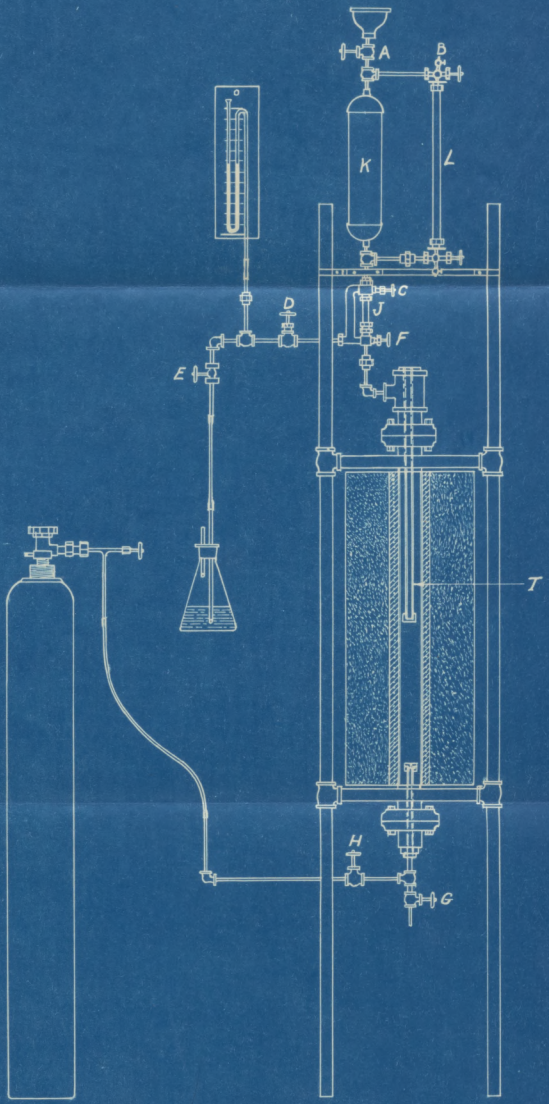


DIAGRAM OF HYDROGENATION APPARATUS

WITH CROSS SECTION OF FURNACE

of external resistance. Temperature was measured with a Hoskins basemetal thermocouple.

When experiments were made in the gaseous state, an iron condenser and receiving flask were connected at the valve H. An outlet for the non-condensable gases and a connection for the eudiometer were provided for on the lower part of the condenser. The hydrogen was admitted at valve D.

When the resrvior has been filled with oil, valves A and B are closed, and the valve C is opened. The hydrogen forces its way through the oil and when there is sufficient pressure above the oil it is forced above down through the sight glass J and into the furnace. The pressure within the furnace is controlled by regulation of the valve E.

In experiments where a catalyist was used, an eight inch brass tube containing the catalyzer was placed in the bottom of the furnace.

4. Methods of analysis. The unsaturation was determined by the sulfuric acid method, but the oil was so dark that a clear separation could not be effected, and when a reading was possible the results did not check. Determination of the Iodine absorption number by the method of the United States Bureau of Chemistry[20] was used as a means of determining the amount of unsaturated compounds, but it is apparently not a reliable method as it would necessarily represent other reactions than simple oxidation in such a complex mixture. Sulfur determinations in the oil were first made by the method of Rothe[21], but it was practically impossible to carry out the necessary evaporation of the excess nitric acid without large losses of sulfur. Sulfur was accurately determined by use of a sulfur bomb, obtaining the sulfur finally as $BaSO_4$.

5. Presentation and discussion of data. The first series of runs were made in the gaseous state at temperature of from 395 to 657°, and without the use of a catalyst. The results of the first six run are as follows:-

Table XII.

Hydrogenation.

	Sp.Gr.	Weight	Temperature	Pressure	Time (minutes)
		Run I.			
Original	0.9779	284			
Product	1.0119	278	595°	1.5"Hg.	25
		Run II.			
Original	0.9779	125			
Product	1.0420	118	600°	1.5"Hg.	20
		Run III.			
Original	0.9779	120			
Product	1.0479	113	657°	2.0"Hg.	27
		Run IV.			
Original	0.9779	109			
Product	0.9880	103	412°	5.0"Hg.	36
		Run VII.			
Original	0.9897	188			
Product	0.9963	175	395°	6.5"Hg.	37
		Run VIII.			
Original	0.9897	135			
Product	0.9980	121	275°	7.5"Hg.	95

From the results obtained it is evident that there was no absorbtion of hydrogen. The specific gravity increases almost directly with the temperature, but the pressure seems to have no effect on it. Three runs were made using catalysts prepared by different methods.

Table XIII.

Hydrogenation with Catalysts.

	Sp.Gr.	Iodine No.	Weight	Temp.	Pressure	Time.
			Run IX.			
Original	0.9897	8.42	335			
Product	1.0173	10.72	322	195°	9.0"Hg.	2 hours 30 m.
			Run X.			
Original	0.9897	8.42	448			
Product	1.0088	11.39	437	200°	9.0"Hg.	2 hours 10min.
			Run XI.			
Original	0.9897	8.42	386			
Product	1.0121	10.42	371	195°	9.5"Hg.	2 hours 20 min

The catalyst for run IX was prepared by reducing nickel nitrate in the furnace under the protection of the oil to be hydrogenated. Pumice stone was used as a carried for the calatyst.

The catalyst for run X was prepared by heating 30 grams of $Ni(NO_3)_2$ in a nickel crucible until most of the water of crystallization was driven off and the salt was in a pasty condition. Small cubes of blowpipe charcol were rolled in the paste until covered by a thin coat of it. The coated cubes were then dried at 110° for two hours. It was then placed in the convertor and heated to 450° for six hours in a slow stream of hydrogen. The temperature was then allowed to drop to 200° and the oil run in from the supply tank and a steady stream of hydrogen passed through the oil.

The catalyst for run XI. was prepared by dissolving 25 grams of $Ni(NO_3)_2$ in an equal weight of water and heating to 80°. 35 grams of pumice were heated in an iron crucible to about 150° and then slowly dumped into an evaporating dish containing the hot solution. As the air and moisture had been largely driven from the pores of the pumice, on coming in contact with the hot liquid

it rapidly drew the same into its pores. The excess water was evaporated and then taken to dryness, with constant stirring. It was then removed to an iron crucible and heated gradually with constant stirring until the water of crystallization and the oxides of nitrogen were being driven off. It was then further heated for fifteen minutes to insure complete oxidation. The mass was then allowed to cool in the air. The material was then placed in the converter and the temperature gradually raised to 280°, as all of the oxide is not reduced at this temperature a final temperature of 340° was reached. During the period of activation, about 6 hours, a slow stream of hydrogen was passed through the converter.

The product from all three runs show an increase in specific gravity, and also as increase in the Iodine number. The increase in the Iodine number would indicate a loss of hydrogen rather than a gain of it.

The sulfur which is present in the oil acts as a poison to the catalyst and its removal was attampted by blowing air through the oil, but only negative results were obtained.

Table XIV.

Sulfur on Oils.

Percent on original oil	1.49 1.49	Percent after 48 hours of air.	1.445 1.54
Percent on original oil	1.28 1.21	Percent after 18 hours of air.	1.21 1.26
Percent on original oil	1.38 1.43	Percent after 24 hours of air.	1.40 1.41

IV. CONCLUSIONS.

1. There are certain natural stopping points in the fractionation of low-temperature tars.

2. The percentage of pitch is low, averaging about 40 percent of the dry tar.

3. The free carbon is low, less than 1.5 percent.

4. The tar acids are high.

5. There are present amounts of sulfur, which poisons any catalyst used to aid hydrogenation.

6. The sulfur cannot be oxidized with air.

7. There is no satisfactory method for determining the amount of unsaturated compounds in coal tar distillates.

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